

Spectral Studies of Hydrogen Bonding and Interaction in the Absorption Processes of COS in Ethylene Aqueous Solution

Jianbin Zhang^{1,*}, Zhenhua Guo¹, Na Zhang¹, Jie Bai¹, Tong Zhang¹, Xionghui Wei^{2,*}

¹College of Chemical Engineering, Inner Mongolia University of Technology, Huhhot 010051;

²Department of Applied Chemistry, College of Chemistry & Molecular Engineering, Peking University, Beijing 100871

Email: tazhang@pku.edu.cn, xhwei@pku.edu.cn

Abstract: In the recent work, absorption data have been measured for COS + N₂ mixture gases in various ethylene glycol (EG) aqueous solutions in the range of (298.15 K to 318.15 K). The measurement shows that the addition of water to EG enhanced the solubility of dilute COS compared with pure EG, and that the 50 % volume fraction of EG in EG aqueous solution (mass fraction is 52.24) is a more reasonable composition used in absorption processes of COS. When conventional UV, FTIR, fluorescence, and ¹H-NMR spectroscopic techniques were used for inspection of spectral changes of COS in EGWs, the spectral results suggest that COS can interact with EG by hydrogen bonds. The results of this work can be used to provide important data for the design and operation of the absorption and desorption processes of COS with potential industrial application of EG aqueous solutions.

Keywords: Hydrogen Bond; Ethylene Glycol; Carbonyl Sulfide; Absorption Process

The removal of carbonyl sulfide (COS) from natural and synthesis gases is a significant operation in industrial processes. The compound is eliminated because of a need to reach specifications imposed in gas transport industries and to respect strict environmental standards^[1]. After COS is the main sulfur compound found in coal-derived gases, and the removal of COS has been largely reported^[2-6].

Ethylene glycol (EG) is an important industrial solvent, which has been used in the absorption processes for SO₂ in the previous works^[7-9] because of its favorable properties, such as low vapor pressure, low toxicity, low viscosity, and low melting point. EG presents native hydrogen bonding sites so that the potential desorption characters are presented in the absorption processes of solutions dissolving gases. Knowledge of the absorption data for dilute COS with EG and EG aqueous solutions (EGWs) under low total pressures is an indispensable requirement for the design of absorption and desorption processes of gases containing COS. But the absorption data are very lack in the current data, so we have to determine the absorption data for COS + N₂ mixtures in

various EGWs for the future industrial application of the solutions containing EG.

In this letter, the absorption data for COS + N₂ in various EGWs at the temperatures of (298.15 to 318.15) K and low pressures were reported to optimize the composition of EGW for the future removal processes of COS. Meanwhile, the work was focused on investigating the possible interaction mechanism of EGW with COS in the absorption processes of COS by FTIR, UV, fluorescence, and ¹H-NMR spectroscopic techniques.

Spectral properties of $\Phi_1 = 50\%$ EGW + COS. The absorption data show that solubility of dilute COS in $\Phi_1 = 50\%$ EGW (mass fraction is 52.24) is the strongest in various EGWs. The interaction between EGW and COS, which is related with the hydrogen bonds among molecules, plays a more important role in the absorption and desorption processes. Therefore, UV and fluorescence spectral changes were used to explore the interactions among EG, H₂O, and COS.

UV spectral changes in the absorption processes of COS in $\Phi_1 = 50\%$ EGW shows that the electronic transitions red shift from 197 nm to 202 nm with increasing COS concentration in EGW. Meanwhile, the UV spectra of pure water with increasing COS concentration keep

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constant. The absorption band at 197 to 202 nm can be due to the $n \rightarrow \sigma^*$ electronic transition of unshared electronic pair of hydroxyl oxygen in EG ^[10] because the $n \rightarrow \sigma^*$ electronic transition of H₂O is often found at the vacuum ultraviolet region, so the spectral shift can be due to the interaction of EG with COS.

Furthermore, the binding character of EGW with COS can be distinguished by examining of the absorption spectrum of the fluorophore. The varieties of the fluorescence excitation and emission spectra of $\Phi_1 = 50\%$ EGW caused by gradually increasing the concentration of COS show that a strong fluorescence excitation spectra of EG at 228 nm in the range of 200-240 nm was observed at an emission wavelength of 307 nm; meanwhile, a strong fluorescence emission spectra of EG at 307 in the range of 300-400 nm was observed at an excited wavelength of 228 nm. The fluorescence emission and excitation spectral intensities of EG decreased with increasing of COS concentration, but not altering the emission maximum and shape of the peaks.

According to overall results, it is expected that the absorption of COS is mainly due to the binding and interaction of EG with COS.

Spectral properties of EG + COS. From above spectral results, the binding and interaction of EG with COS play important role in the absorption of dilute COS, so the UV, IR, fluorescence, ¹H-NMR spectra were determined to investigate the binding and interaction.

The characteristic band of EG was identified in UV spectra, but no information on a complexing reaction could be obtained. With increasing COS concentration, the special absorption band shifts from 200 nm to 207 nm and the absorption intensity increases. The shift can be due to the addition of COS, which destroys the original hydrogen bonding and interaction among EG molecules and forms the new hydrogen bonding and interaction of hydroxyl hydrogen atoms in EG with oxygen atoms in COS.

The binding of EG with COS can be distinguished by examining of the absorption spectrum of the fluorophore. The Collisional quenching only affects the excited states of the fluorophores, thus no changes in the absorption spectrum are predicted. In contrast, the ground state

binding formation will frequently result in perturbation of the absorption spectrum of fluorophore. The fluorescence excitation and emission spectra of fluorophore can be treated as the same as the absorption spectra of the fluorophore. The quenching of the intrinsic fluorescence excitation and emission spectra of EG caused by gradually increasing the concentration of COS were mainly related to $\sigma^* \rightarrow n$ electron transition of oxygen atom in EG. The quenching phenomenon can be due to the addition of COS, which destroys the original hydrogen bonding and interaction among EG molecules and forms the new hydrogen bonding and interaction of EG with COS.

The recorded IR spectra of EG + COS show that one stretching band is observed at 1704 cm⁻¹, which can be attribute to the stretching vibrational band of C=O (*V*'s) in COS because the IR spectra indicate that the fundamental frequencies of the stretching band of C=O often are found in the range of (1710 to 1820) cm⁻¹ ^[11]. However, the observed IR value is lower than the reference values. The phenomenon could be due to that the addition of COS forms the new hydrogen bonding and interaction of hydroxyl hydrogen atom in EG with oxygen atom in COS.

The ¹H-NMR spectral result of EG shows that the chemical shifts of hydrogen in -CH₂- appear at $\delta = 3.390$ to 3.403 ppm (4H), and the chemical shift of hydrogen in -OH appears at $\delta = (4.461$ to 4.489) ppm (2H) in the ¹H-NMR spectrum of pure EG. In the presence of COS, however, there appears at $\delta = (3.381$ to 3.419) ppm (4H) and (4.470 to 4.498) ppm (2H). Meanwhile, the chemical shift of hydrogen atoms in -OH group shifts from $\delta = (4.461$ to 4.489) ppm to (4.470 to 4.498) ppm, which was due that the bond length of O-H in EG molecules become longer and the electron cloud of hydrogen atoms in EG become thinner. The results show that there is hydrogen bonds between EG and COS so that shielding effect from oxygen atoms of COS makes the signal move to lower magnetic field.

The above results suggest the hydrogen bonding and interaction between hydroxyl hydrogen atoms in EG molecules and oxygen atoms in COS molecules occurred. When such hydrogen bonds are formed, hydroxyl hy-

drogen atoms in the EG molecules are attracted by the oxygen atoms in COS and the bond length between hydrogen atom and oxygen atom in EG molecules are elongated. In this situation, the $n \rightarrow \sigma^*$ electron transition of oxygen atom in EG become more easily, so red shift phenomena occurred.

According to overall results, it is expected that hydrogen bonding and interaction among molecules is formed as $\cdots \text{HO}-\text{CH}_2\text{CH}_2\text{O}-\text{H} \cdots \text{OCS}$. The hydrogen bonding and interaction makes the desorption of COS from EGW occur easier. The hydrogen bonding and interaction of oxygen atom in COS with hydroxyl hydrogen atom in EG is very useful to desorb COS from EGWs by pressure reduction, by temperature rise, and by use of a carrier gas.

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